

Supplementary Information

Furan-Containing Conjugated Polymer for High Mobility Ambipolar Organic Thin Film Transistors

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Experimental

General

All the chemicals were purchased from Sigma-Aldrich, Strem, Acros and used without further purification. All reactions were carried out using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents. 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-octyl-1-dodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole were synthesized according to the reported procedure.^{1,2}

Characterization

¹H and ¹³C NMR data were performed on a Bruker DPX 300 MHz or 400 MHz spectrometer using solvent CDCl₃. The chemical shifts were recorded in ppm using TMS as an internal standard. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument using dithranol as a matrix. Gel Permeation Chromatography (GPC) analysis against polymethylmethacrylate (PMMA) standards was performed in THF + Chloroform solvent mixture at 40 °C on a Waters high pressure GPC assembly with an M590 pump (model 2690), μ- Styragel columns of 105, 104, 103, 500 and 100 Å and a refractive index (RI) detector. A typical concentration 1.5 mg weight of polymer dissolved in 1 ml of THF was used for running GPC samples. UV-Vis spectra were recorded on a Shimadzu model 2501-PC. Cyclic voltammetry experiments were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. All CV measurements were recorded in solid state with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte (scan rate of 100 mV.s⁻¹). The experiments were performed at room temperature with a conventional three-electrode configuration consisting of a platinum disc working electrode, a gold counter electrode, and an Ag/AgCl reference electrode using ferrocene/ferrocinium ion as internal standard. The working platinum electrode was coated with the polymer thin film by using a polymer solution in chloroform. The HOMO and LUMO energy levels were calculated using the equation $E_{\text{HOMO}} = E_{\text{ox-onset}} + 4.4 \text{ eV}$ and $E_{\text{LUMO}} = E_{\text{red-onset}} + 4.4 \text{ eV}$ where $E_{\text{ox-onset}}$ is the onset potential for oxidation relative to the Ag/AgCl reference electrode. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument

(scanning rate of 10°C min⁻¹). Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 instrument (heating rate of 10°C min⁻¹).

Synthesis of 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1): Sodium (5.17 g, 0.225 mol) was added to a three-neck flask containing 2-methyl-1-butanol (90 mL) under argon. The mixture was heated to 90 °C and FeCl₃ (65 mg) was added. After complete disappearance of sodium, then the solution was cooled to 85°C. 2-Furonitrile (13.96 g, 0.15 mol) was added to the reaction mixture, followed by drop-wise addition of diisopropyl succinate (12.15 g, 0.06 mol) in 2-methyl-1-butanol (8 mL) over 1 h at 85 °C. When the addition was completed, the mixture was stirred for additional 2 h at this temperature. The reaction mixture was then cooled to 50°C, diluted with methanol (65 mL), and then slowly neutralized with glacial acetic acid (~25 mL) and refluxed for 15 min. The reaction mixture was cooled down to room temperature and filtered. The solid was washed respectively with hot methanol and de-ionized (DI) water several times, and dried in vacuo at 50°C. A dark red solid was obtained. Yield: 9.00 g (60.0%).

Synthesis of 2,5-bis(2-octyl-1-dodecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione: Compound 1 (4.0 g, 14.90 mmol) and anhydrous K₂CO₃ (6.17 g, 44.70 mmol) were added to a dry 250 ml three-neck round bottom flask and kept it under vacuum at 50 °C for one hour then anhydrous N, N-dimethylformamide (DMF) (300 ml) was added under argon to the above mixture. This mixture was then heated to 120°C under argon for 1h. 2-Octyl-1-dodecylbromide (16.15 g, 44.70 mmol) was added drop-wise, and the reaction mixture was further stirred overnight at 130°C. The reaction mixture was allowed to cool down to room

temperature next day and poured into water (600 mL) and stirred for 30 min. The product was extracted with chloroform, washed with DI water, and dried over anhydrous MgSO_4 . Removal of the solvent afforded the crude product which was further purified using column chromatography on silica gel (a mixture of hexane and chloroform as eluent) to give the product as a red solid (5.0 g, 40%). ^1H NMR (400 MHz, CDCl_3): δ 0.86 (t, $J = 6.4$ Hz, 12 H), 1.15 -1.40 (m, 64 H), 1.79 (s, 2 H), 4.01 (m, 4 H), 6.68 (dd, $J = 1.4$ Hz, 1.6 Hz, 2 H), 7.59 (s, 2 H), 8.32(d, $J = 3.6$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.89, 146.25, 132.82, 126.16, 122.17, 115.48, 106.36, 46.65, 38.80, 31.90, 31.87, 31.48, 30.09, 29.62, 29.61, 29.54, 29.49, 29.32, 29.27, 26.48, 22.65, 22.63, 14.05. MS (MALDI-TOF, m/z): calcd. for $\text{C}_{54}\text{H}_{88}\text{N}_2\text{O}_4$, 828.67; found, 828.53 (M).

Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-octyl-1-dodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2): 2,5-bis(2-octyl-1-dodecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4.0 g, 4.82 mmol) and chloroform (40 mL) were charged to a 100 mL three neck flask equipped with a stirring bar, a condenser, and a dropping funnel. Bromine (Br_2) (0.50 mL, 9.64 mmol) in chloroform (20 mL) was then added drop wise to the flask at room temperature through the dropping funnel. The mixture was stirred at room temperature overnight, then slowly poured to an aqueous solution of sodium thiosulfate and stirred for additional 30 min. The product was extracted with chloroform, then washed with DI water, and dried over anhydrous MgSO_4 . Removal of the solvent afforded the crude product which was further purified using column chromatography on silica gel (a mixture of hexane and chloroform as eluent) to give the product as a dark red solid (3.50 g, 73%). ^1H NMR (400 MHz, CDCl_3): δ 0.85 (t, $J = 6.2$ Hz, 12 H), 1.10-1.40 (m, 64 H), 1.76 (s, 2 H), 3.96 (d, $J = 6.7$ Hz, 4 H), 6.59 (d, $J = 3.4$ Hz, 2 H), 8.27 (d, $J = 3.4$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.87, 146.23, 132.78, 126.13, 122.14, 115.45, 106.34, 46.63, 38.78, 31.87, 31.84, 31.47, 30.07, 29.59, 29.52, 29.46, 29.29, 29.24, 26.46, 22.62, 14.02. MS (MALDI-TOF, m/z): calcd. for $\text{C}_{54}\text{H}_{86}\text{Br}_2\text{N}_2\text{O}_4$, 984.50; found, 986.38 (M+2).

Synthesis of 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole

(4): 4,7-Dibromo-2, 1, 3-benzothiadiazole (3) (4.0 g, 13.6 mmol), bis(pinacolato)diboron (8.0 g, 31.2 mmol), PdCl₂(dppf) (2.0 g, 2.4 mmol), and KOAc (8.0 g, 80 mmol) was kept under vacuum for 10 min and then degassed before 1,4-dioxane (50 mL) was added under argon. The reaction mixture was stirred at 80 °C overnight and quenched by adding water. The resulting mixture was extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and filtered. After removing the solvent, a dark red solid was obtained, which was purified by silica gel chromatography by using 3 % ethyl acetate in hexane as eluent to give the title compound as a pink solid (2.4 g, 46 %). ¹H NMR (400 MHz, CDCl₃): δ 8.12 (s, 2H), 1.43 (s, 24H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 157.55, 138.11, 84.91, 25.3. Anal. Calcd for C₁₈H₂₆Br₂N₂O₄S: C, 64.51; H, 5.73; N, 4.43; S, 25.33. Found C, 64.81; H, 5.92; N, 4.76; S, 25.25. MALDI-TOF-MS (dithranol) m/z: = 388.0; calcd. for C₁₈H₂₆B₂N₂O₄S = 388.18.

Synthesis of poly{3,6-difuran-2-yl-2,5-di(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4-dione-alt-benzothiadiazole} (PDPP-FBF):

To a 50 mL Schlenk flask, 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-octyl-1-dodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.400 g, 0.40 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (0.157 g, 0.40 mmol) were dissolved in toluene (10 mL). 2M K₂CO₃ (5 mL) and 2 drops of Aliquat 336 were added in the above reaction mixture. The solution was purged with argon for 30 min, and then tetrakis(triphenylphosphine)palladium (20 mg, 0.017 mmol) was added. The reaction was stirred at 80°C for 3 d. Then a solution of

phenylboronic acid was added, followed by the addition of bromobenzene and stirred overnight. The resulting mixture was poured into a mixture of methanol (100 mL) and water (100 mL) and stirred overnight. The precipitated dark solid was filtered off and re-dissolved in chloroform and added drop wise to methanol (250 ml). The resulting solid was filtered off and subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), and hexane (24 h), respectively. The residue was finally extracted with chloroform and precipitated again from methanol, filtered, washed with methanol, and dried under vacuum (74 % yield).

M_w/M_n (GPC) = 455,300/ 219,600, polydispersity index (PDI) =2.07, λ_{max} (UV-vis-Near IR): 880 nm (in chloroform); 778 nm (thin film). Absorption cutoff from thin film= 980 nm.

OTFT Fabrication and Characterization

Top contact/bottom gate OTFT devices fabricated using p+-Si/SiO₂ substrates where p+-Si and SiO₂ work as gate electrode and gate dielectric, respectively. The thickness of thermally grown silicon oxide layer is around ~200 nm with a capacitance of about 15 nF/cm². Substrates were cleaned using ultrasonication in acetone, methanol and de-ionized water. The cleaned substrates were dried under a nitrogen flow and heated at 100°C for 5 min. The substrates were then treated in UV-ozone for 20 min. Then, the substrate was kept in a desiccator with a few drops of octyltrichlorosilane (OTS). The desiccator was evacuated for 3 min and placed in an oven at 110 °C for 3 hr. The substrate was removed from the desiccator, thoroughly rinsed with isopropanol, and dried under a nitrogen flow. PDPP-FBF polymer thin film was deposited via spin coating using 8 mg/ml solution in chloroform on the OTS treated Si/SiO₂ substrate. Subsequently, on top of the polymer active layer, a roughly 100 nm thick Gold (Au) thin film was deposited for Source (S) and Drain (D) electrodes through a shadow mask. For a typical OTFT device reported here, the source-drain channel length (L) and channel width (W) was 180 μm and 3 mm, respectively. The device characteristics of the OTFTs were measured at room temperature under nitrogen with a Keithley 4200 source meter. The field effect mobility (μ) was calculated from the saturation regime of transfer characteristics.

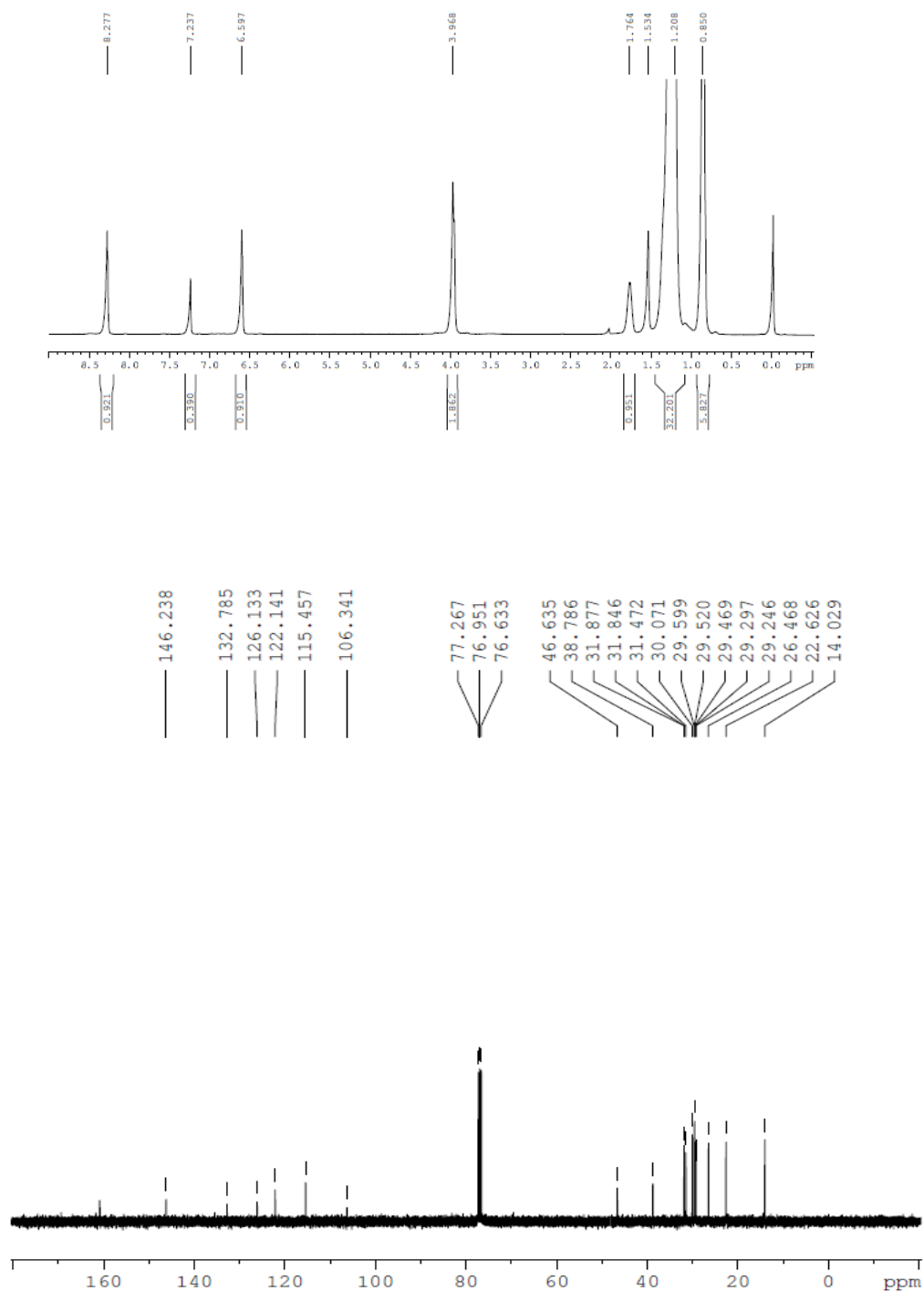


Figure S1. ¹H NMR and ¹³C spectrum of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-octyl-1-dodecyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione in CDCl₃ (**2**).

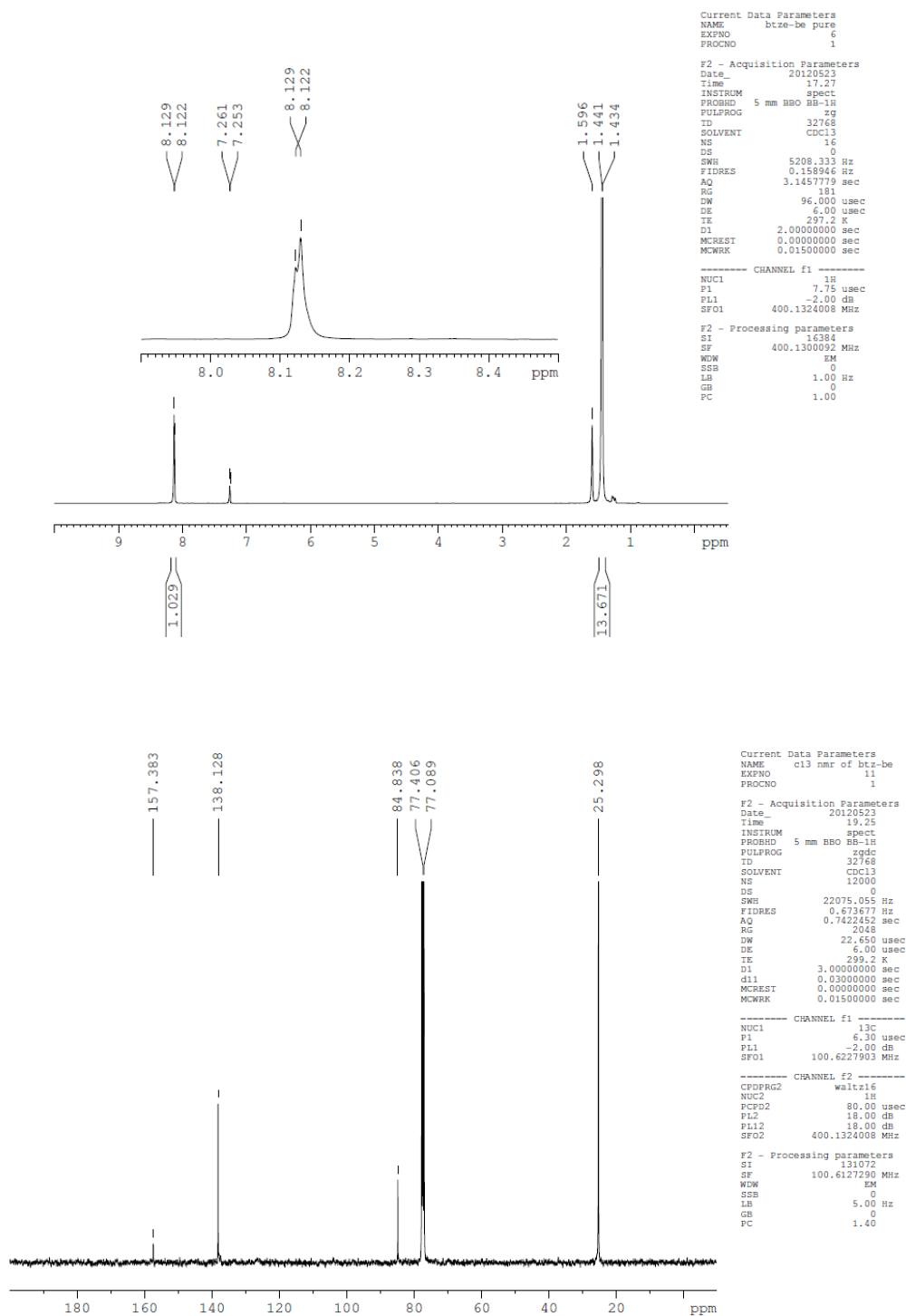


Figure S2. ^1H NMR and ^{13}C spectrum of 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (**4**).

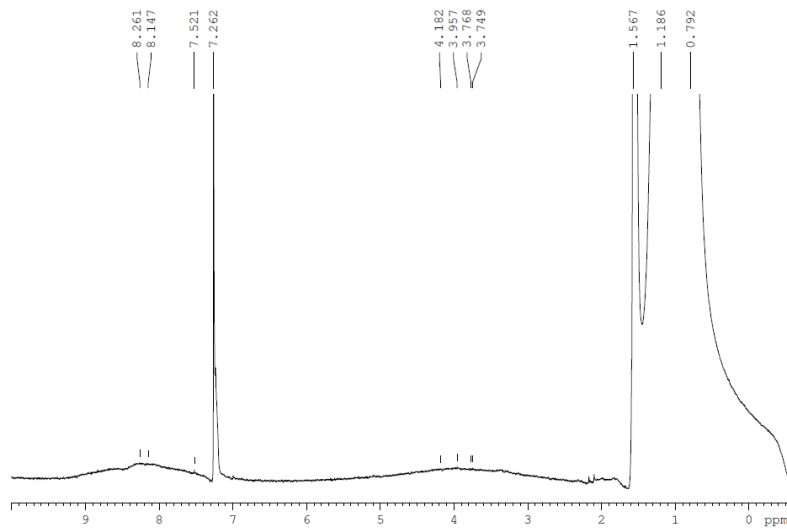
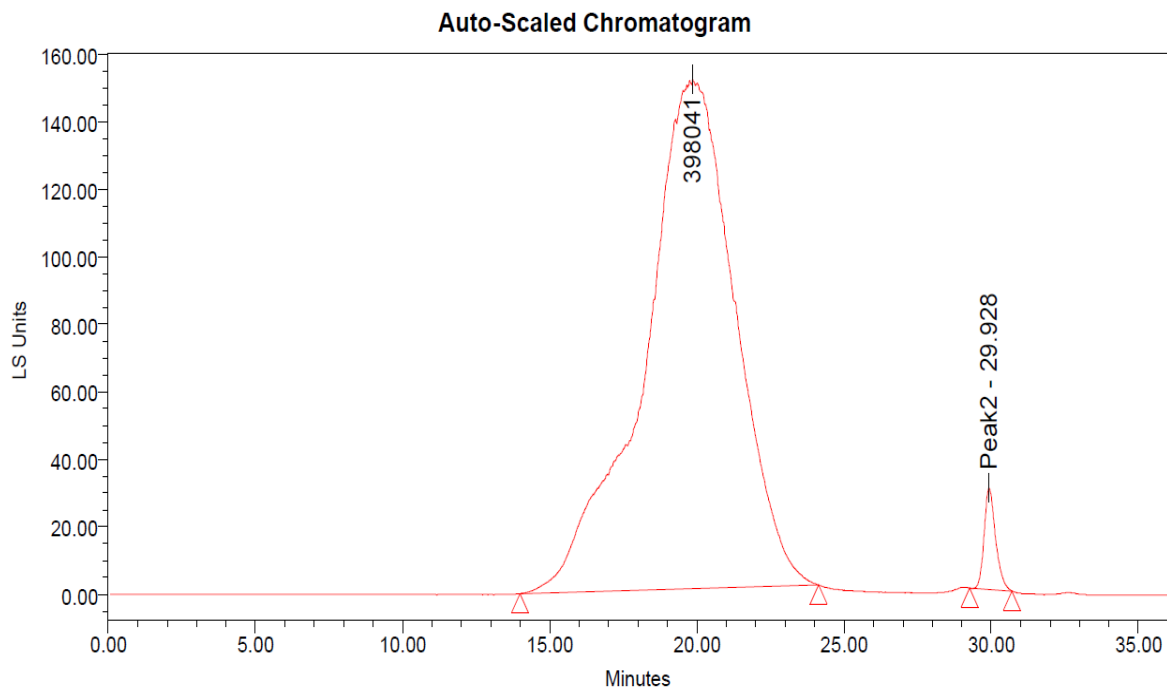


Figure S3. ¹H NMR spectrum of poly{3,6-difuran-2-yl-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-alt- benzothiadiazole} (PDPP-FBF).



Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	219604	455346	398041	755337	1000815		2.073491		
2									

Figure S4. Gel permeation chromatogram of polymer **PDPP-FBF** in THF and Chloroform using PMMA internal standard.

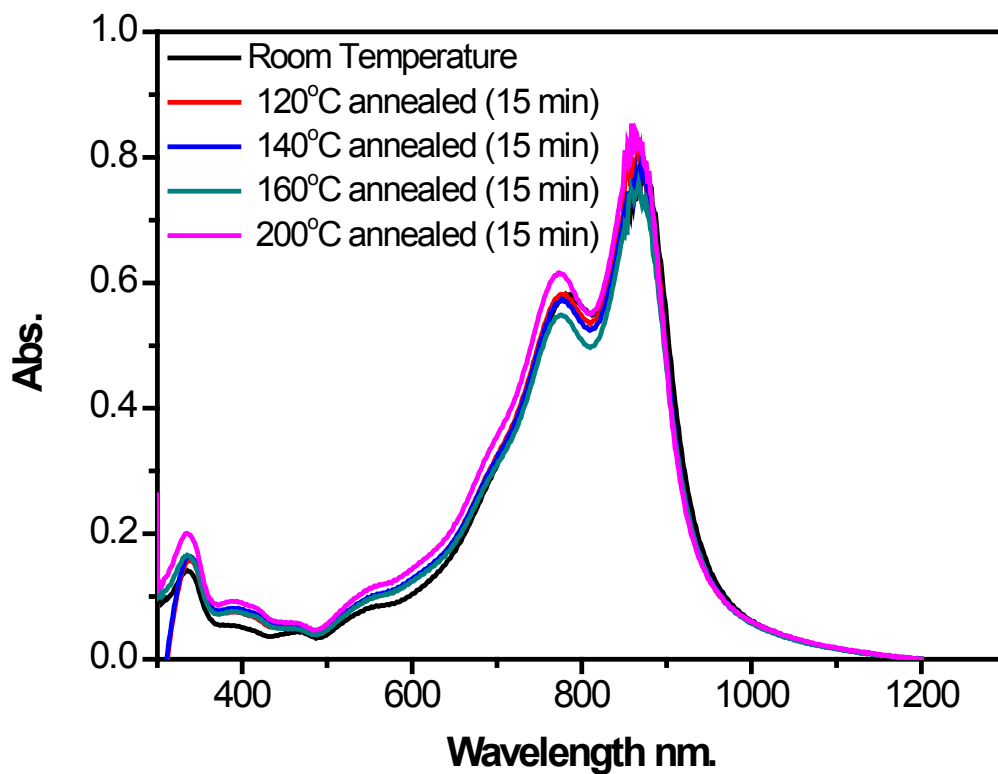


Figure S5. Effect of annealing at various temperatures on solid state absorption of **PDPP-FBF** thin films processed using chloroform solution.

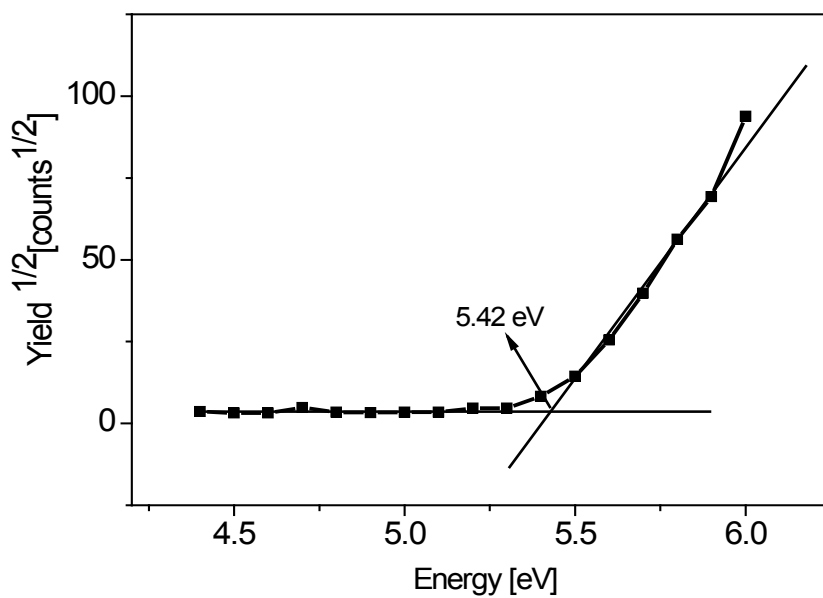


Figure S6. Photoelectron spectroscopy in air (PESA) measurements of **PDPP-FBF** copolymer thin film spin coated on glass substrate.

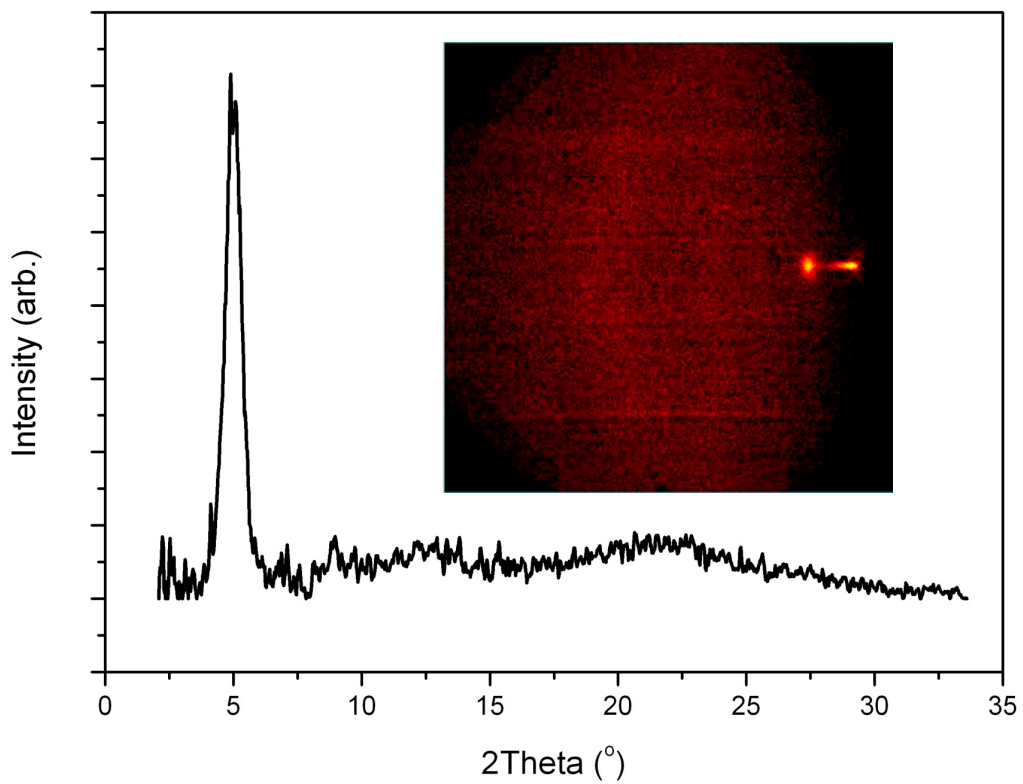


Fig. S7 XRD diffraction pattern and diffractogram for **PDPP-FBF** microstrips obtained when preannealed thin film deposited at 200°C on OTS modified SiO₂/Si substrates.

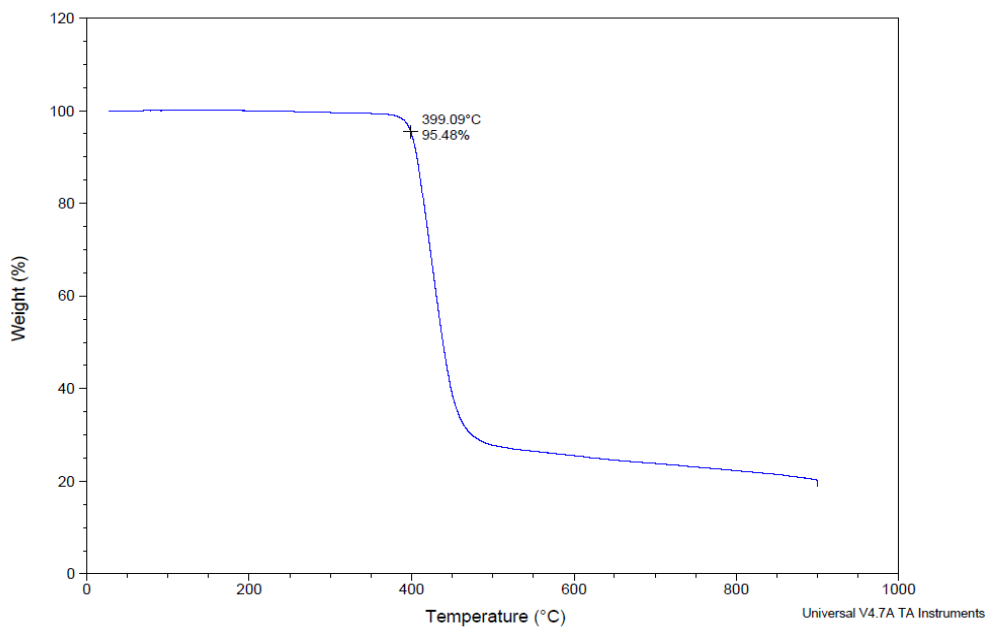
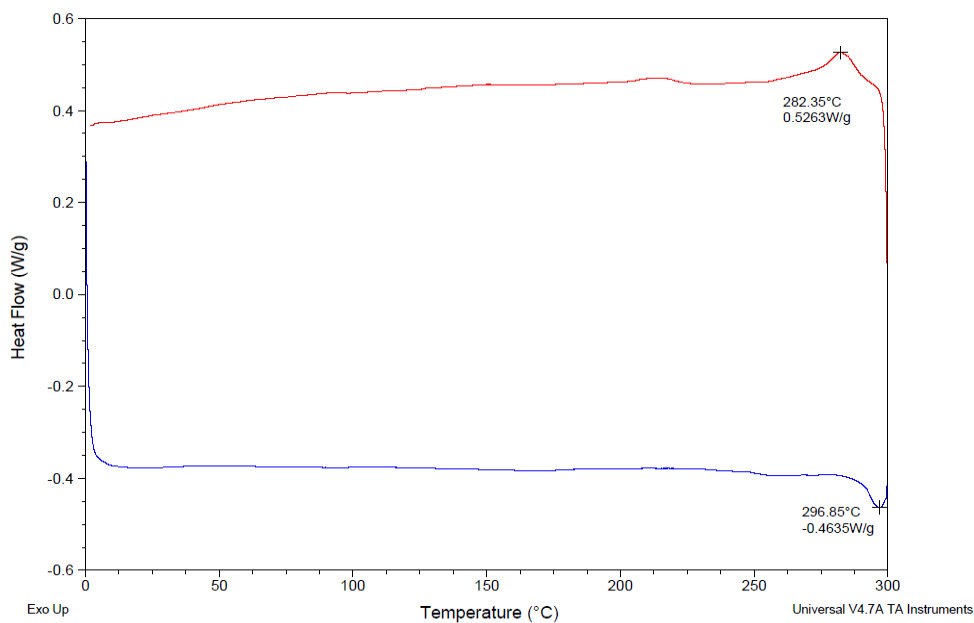


Fig. S8 Differential Scanning Calorimetry (DSC) and thermo gravimetric analysis (TGA) of **PDPP-FBF** polymer.

References

1. Y. Li, P. Sonar, S. P. Singh, W. Zeng, M. S. Soh, *J. Mater. Chem.* 2011, **21**,10829.
2. M. Zhang , H. N. Tsao ,W. Pisula , C. Yang , A. K. Mishra , K. Müllen , *J. Am. Chem. Soc.* 2007 , 129 , 3472.